Removal of dissolved metals by activated carbon from road runoff in batch systems – equilibrium and kinetic*

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Abstract: *Removal of dissolved metals by activated carbon from road runoff in batch systems – equilibrium and kinetic.* Activated carbon is an effective sorbent for removing organic and inorganic contaminants from aqueous solutions. In conducted experiments, granulated activated carbon (GAC) was used to examine the adsorption processes of heavy metals (Cd, Cu, Ni, Pb and Zn). Studies (performed in batch system) were carried out as a function of time, heavy metals concentration and pH values. The obtained results show that GAC effectively removes mentioned metals. Numerous kinetic models were used to investigate the mechanism of adsorption processes. Using the Langmuir isotherm, the maximum adsorption capacities were calculated to be 3.010, 3.662, 4.430, 3.800 and 4.169 mg·g^{-1} for Cd, Cu, Ni, Pb and Zn, respectively, in neutral conditions and 2.684, 2.578, 3.482, 2.592 and 2.253 mg·g^{-1} in acidic conditions.

Key words: activated carbon, heavy metals, road runoff, adsorption

INTRODUCTION

One of the significant sources of contamination are road infrastructure and transport. During rainfall, a wide range of substances, including heavy metals, polycycling aromatic hydrocarbons (PAHs), de-icing agents, oil, grease and sediments are washed from roads into surface and groundwater (Béchet et al. 2010, Fach and Dierkes 2011). A wide range of metals have been detected in runoff of those the most commonly reported are Cd, Cu, Ni, Pb and Zn (Blecken et al. 2012). Acid precipitation (acid rain) are strictly dependent on transport pollution such contaminants as oxides of nitrogen (NO_x) and sulphite (SO_2). Acid rain (having a pH level of less than 5.6) is caused by nitric and sulphur acids formed by mixing of NO_x and SO_2 with moisture/vapour in the atmosphere. The NO_x and SO_2 gases are produced during a variety of industrial, mine processes (e.g. fossil fuels) and transport. Soil by buffering capacity may have neutralized some of the acidity of the acid rainwater. On the other hand, the environmental degradation may cause rapid decrease of soil pH and in consequence accelerate soil weathering and remove nutrients (GAO 13-39 2013). Moreover, in more acidic environment some toxic elements, for example heavy metals, become more soluble and might migrate for long distance from the source. These phenomena

depends on metal bonding forces of the soil particles and on dissolving action of hydrogen ions, which can break down rocks and soil particles. Heavy metals are the contaminants of grates anxiety, because they are non-biodegradable and toxic for environment. Therefore, remediation of these pollutants is a great challenge. To protect the environment in the vicinity of roads different systems might be implemented such as collection basins, wetland systems, oil separators and bioremediation techniques (Gotvajn and Zagorc-Končan 2009, Kluge and Wessolek 2012). Several research studies have found significant levels of heavy metals, such as Cd, Cu, Ni, Pb, and Zn in urban stormwater, which the median values of concentrations were as follows (in mg·L^{-1}): 0.009–0.100 for Cd, 0.006–0.100 for Cu, 0.008–0.020 for Ni, 0.008–1.900 for Pb, 0.06–19.100 for Zn (Davis et al. 1999, Davis and Birch 2001, Kayhanian et al. 2003, Barrett et al. 2006, Kayhanian et al. 2007; Barrett 2008, Lau et al. 2009). However, in this case the typical water purification methods (e.g. chemical precipitation, reduction, adsorption, osmosis etc.) could be implemented. In general, those methods are very expensive and energy-intensive, as well as demand large quantities of chemical reagents. Among these, adsorption onto granular activated carbon (GAC) in treatment zone of permeable reactive barrier seems to be a potential alternative and may become an efficient and relatively low-cost technology. GAC is widely used for dechlorination, industrial wastewater conditioning (Zayat and Smith 2010) and groundwater re-

mediation – permeable reactive barriers (Roehl et al. 2006). A number of studies confirm that activated carbon might be wildly used for heavy metals removal, i.a., Sulaymon et al. (2012), Liu et al. (2013) and Venkatesan et al. (2013). The aim of these studies was to evaluate the application possibility of GAC granular activated carbon as a reactive media for road runoff purification. Sorption test, including batch equilibrium and kinetic tests, were carried out using multicomponent heavy metals solution. Experimental data based on measurements of chemical analyses of solutions after tests have been fitted to different models – two kinetic and three isotherm models previously reported in literature.

MATERIAL AND METHODS

Adsorbent and adsorbates

Granular activated carbon (GAC) used in the tests was obtained from Active Carbon Research and Production Company, Mrozy, Poland. Its particle size, specific gravity and bulk density were 0.40–1.00, 1.96 and 0.45 mm, respectively. Moreover, surface area and porosity analyzer (ASAP 2020M Micromeritics, USA), scanning electron microscope (SEM) images (FEG Quanta 250, USA) and X-ray diffraction (Philips X'Pert APD, the Netherlands) spectra were used to detailed characterization of GAC particles.

All tests were performed using a dilute solutions simulated the road runoff. The solutions were prepared by mixing 5 mL of distilled water and required quantity of analytical reagent grade of

cadmium, copper, nickel, lead and zinc (6.7 mL for kinetic tests and 0.1, 0.2, 0.5, 1.0, 1.5, 2.0, 2.5, 4.0, 5.5, 7.0, 8.5, 10.0 mL for equilibrium tests) and then diluted to 100 mL with distilled water. The concentrations used in presented investigations were higher than a maximal allowable concentration (MAC) for groundwater in Poland (Polish Journal of Laws from 2006, No 137, item 984 as amended).

Batch sorption test

The kinetic and equilibrium tests were carried out using 2 g of GAC and 100 mL of aqueous solutions. Batch kinetic experiments for 67 mg·L^{-1} mixed metal solution were conducted to evaluate the uptake rates and contact times needed to achieve equilibrium. To determine the time in which the adsorption equilibrium under static conditions occurs, a set of sorption measurements of metal concentration in the multicomponent solution were undertaken after 1, 3, 6, 10, 24 and 48 h. In equilibrium tests the initial concentrations of metals were vasried from 0 to 100 mg·L^{-1} and the contact time was 48 h. Aqueous solution without adsorbates were used as control samples. The double-blind tests and the other aqueous solutions containing mixtures of Cd, Cu, Ni, Pb, Zn and reactive material were placed into 250 mL bottle made of polyethylene. Before tests, the values of pH, temperature and electrical conductivity were measured using a portable instrument pH/conductivity meter (SCHOTT, Germany). The samples were then placed into rotary shaker (GFL, Germany) set at 15 rpm for time required for different type of batch tests, after which pH, temperature and conductivity values were measured. The tests were performed in duplex at laboratory temperature of 20–22°C. Before chemical analyses the solution was centrifuged at 3,000 rpm for 5 min. The final concentrations of the heavy metal ions in the solution were measured by plasma – atomic absorption spectroscopy ICP-AAS (Thermo Scientific, USA). The unit adsorption amount and the removal ratio of heavy metals R(%) were calculated by (Michel and Kiedryńska 2011):

$$q_t = \frac{(C_0 - C_e) \cdot V}{m}$$

and

$$R(\%) = \frac{C_0 - C_t}{C_0} \cdot 100\%$$

where:
q_t – unit adsorption amount (mg·g^{-1}),
C_0, C_e, C_t – initial, equilibrium and final concentrations of heavy metal ions, respectively (mg·L^{-1}),
V – volume of the aqueous solution (L),
m – mass of adsorbent (mg).

For kinetic tests data interpretation the following models were used: pseudo-first and pseudo-second order kinetics models and intraparticle diffusion model. Formulas of the applied models are presented in Table 1.

Equilibrium tests results were analyzed using Langmuir, Redlich-Peterson and Temkin isotherm models. The equations of the applied isotherm models are presented in Table 2.

TABLE 1. The kinetic models

Model	Equation	Plot
Pseudo-first order (Ho and McKay 1999, Ho 2006)	$\log(q_e - q_t) = \log(q_e) - \dfrac{k_{p1}t}{2.203}$	$\log(q_e - q_t)$ vs. t
Pseudo-second order (Ho 2006, Ibrahim et al. 2013)	$\dfrac{t}{q_t} = \dfrac{1}{k_{p2}q_e^2} + \dfrac{t}{q_e}$	$\dfrac{t}{q_t}$ vs. t
Intraparticle diffusion (Alkan et al. 2007)	$q_t = k_{int} \cdot t^{1/2}$	q_t vs. $t^{1/2}$

Where: q_e is the equilibrium adsorption capacity of the copper ions (mg·g^{-1}); q_t is the adsorption capacity determined after time t (mg·g^{-1}); k_{p1} and k_{p2} are the equilibrium rate constants of the pseudo-first order model (min^{-1}) and pseudo-second order model (g·mg^{-1}·min^{-1}), respectively; k_{int} is the intraparticle diffusion rate constant (mg·g^{-1}·min$^{-1/2}$).

TABLE 2. The isotherm models

Isotherm	Non-linear form	Linear form
Langmuir (Langmuir 1916)	$q_e = \dfrac{q_{max} \cdot K_L \cdot C_e}{1 + K_L \cdot C_e}$	$\dfrac{C_e}{q_e} = \dfrac{C_e}{q_{max}} + \dfrac{1}{K_L \cdot q_{max}}$
Temkin (Temkin and Pyzhev 1940)	$q_e = B \cdot \ln(A \cdot C_E)$	$q_e = B \cdot \ln A + B \cdot \ln C_e$
Redlich-Peterson (Redlich and Peterson 1959, Jossens et al. 1978)	$q_e = \dfrac{K_R \cdot C_e}{1 + b_R \cdot C_e^{\beta}}$	$\ln\left(K_R \cdot \dfrac{C_e}{q_e} - 1\right) = g\ln(C_e) + \ln(b_R)$

Where: q_e is the adsorption capacity (mg·g^{-1}); K_L is the Langmuir adsorption constant related to the affinity of the binding sites (L·mg^{-1}); q_{max} is the maximum amount of heavy metal ions per unit mass of adsorbent when all bindings sites are occupied (mg·g^{-1}); C_e is equilibrium concentration of heavy metals (mg·L^{-1}); A is the Temkin isotherm equilibrium binding constant (L·mg^{-1}); B is the Temkin isotherm equilibrium constant; K_R (L·mg^{-1}), b_R (L·mg^{-1}) and β are Redlich-Peterson isotherm constants.

Character of adsorption processes may be determined using a dimentionless constant commonly known as separation factor – R_L (Hall et al. 1966):

$$R_L = \frac{1}{1 + K_L \cdot C_0}$$

When R_L is between 0 and 1 Langmuir isotherm is favourable, for R_L above 1 adsorption nature is unfavourable, for R_L equal to 1 adsorption has linear form and is irreversible when R_L equals 0.

RESULTS AND DISCUSSION

Characterization of the adsorbent

Figure 1 represents the XRD pattern and scanning electron images of GAC sample. Pattern and increased values of background [15-35 (2Θ)] on XRD spectra of the sample shows, that the dominant mineral component is amorphous substance characteristic for activated carbons. The characteristic interplanar spacing (4.255, 3.344, 2.456, 2.283, 2.237, 2.128, 1.981 Å) attributed
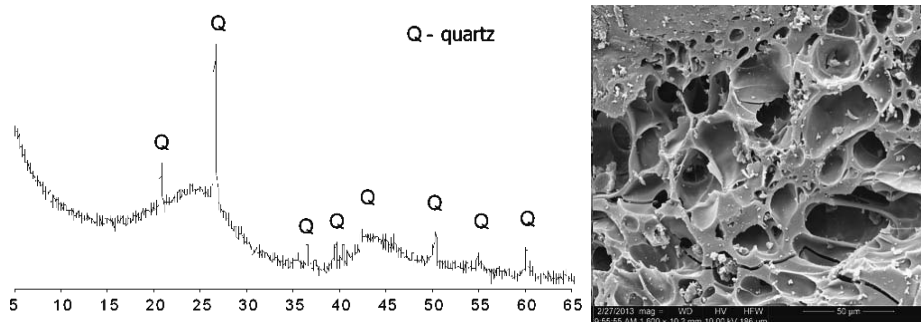
FIGURE 1. The XRD pattern and SEM images of the granular activated carbon sample

to quartz as an additional mineral component of the sample. The observations of microstructure lead to the conclusion that the surface of reactive material was highly porous and rough. The pores were circular in shape and were dissimilar in size (from 10 to 300 µm).

The reactive material is characterized by extraordinary specific surface area, which was determined at 856 $m^2 \cdot g^{-1}$. The total pore volume of GAC was 0.4268 $mL \cdot g^{-1}$.

Kinetic tests

In kinetic test the low pH values of initial solutions were predicted due to less favorable conditions – the lower intensity of adsorption processes. Based on the removal ratio (Table 2), the equilibrium time required for adsorption of heavy metals on granular activated carbon was determined to be about 48 h. The obtained data indicate that the adsorption processes were slow and evenly distributed over time. The unit adsorption amount of heavy metals (Cd, Cu, Ni, Pb, Zn) slowly increases until it reaches maximum level after 48 h. The final removal ratios were as follows 45.62% for Cd, 61.12% for Cu, 59.91% for Ni, 65.13% for Pb and 41.87% for Zn. Apparently, low reduction of previously mentioned metals was due to low pH values of initial solutions (Srivastava et al. 2007). Predicted parameters of sorption kinetics are shown in Table 3 and graphical interpretation of the test results are shown in Figures 2 and 3.

TABLE 3. Effect of contact time on heavy metals removal by adsorption onto granulated activated carbon

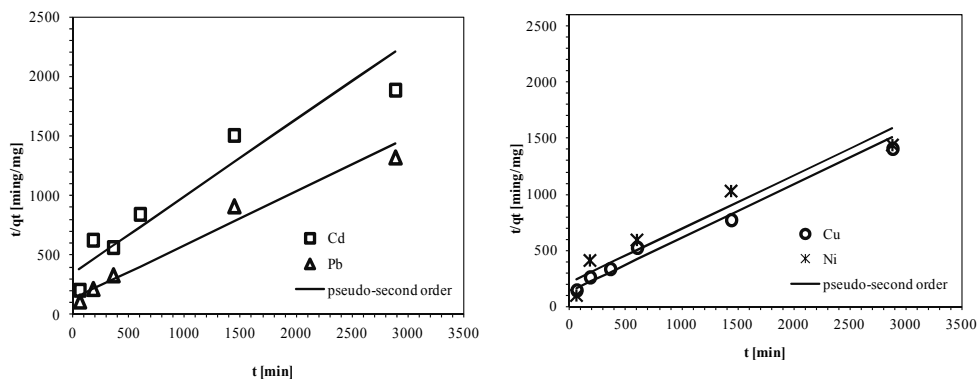| Contact time (h)	Removal ratio of Cd (%)	Removal ratio of Cu (%)	Removal ratio of Ni (%)	Removal ratio of Pb (%)	Removal ratio of Zn (%)
1	8.75	12.49	19.05	16.19	5.39
3	8.59	20.63	13.22	24.94	4.56
6	19.07	32.12	–	32.52	15.14
10	21.26	34.18	30.42	–	24.81
24	28.57	55.78	41.94	47.27	21.69
48	45.62	61.12	59.91	65.13	41.87

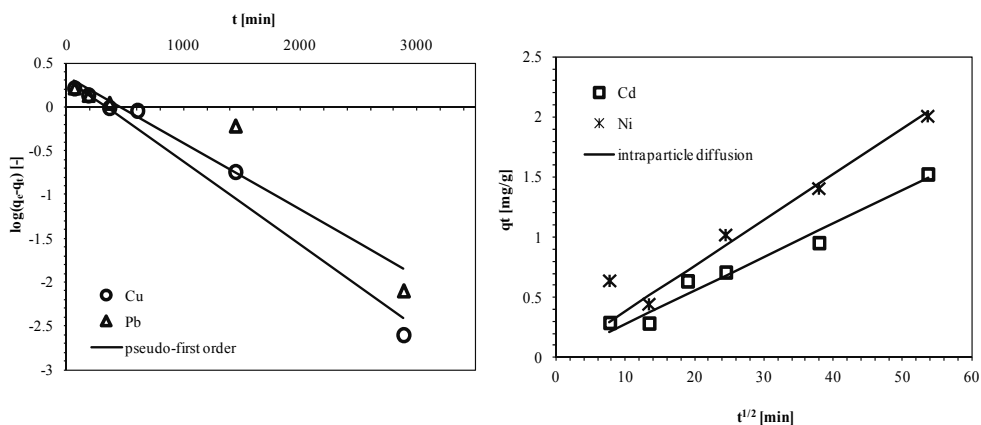FIGURE 2. Fitting test data with the pseudo-second order kinetic model

FIGURE 3. Fitting test data with the pseudo-first order kinetic model and the intraparticle diffusion model

According to the correlation coefficient R^2, the obtained data were well fitted to pseudo-second order kinetic model. The coefficients of determination (R^2) for all the ions present in solution (Cd, Cu, Ni, Pb and Zn) were as follows 0.909, 0.989, 0.969, 0.969 and 0.721 (Table 4). The kinetics reaction of the active carbon is usually described by the pseudo-second order model, which is confirmed by several studies, including: Ho and McKay (1999), Rivas et al. (2005), Sulaymon et al. (2012). The pseudo-second order model is based on the processes of chemisorptions and the

assumption that the limiting factor may be electrostatic and intermolecular forces between the adsorbent and adsorbate (Ho and McKey 1999, Ho 2006). The pseudo-second order kinetic parameters indicate that the copper, lead and nickel ions were removed from the solution in the greatest extent.

The test results for heavy metals removal were also plotted using pseudo-first order kinetic model and intraparticle diffusion model. The models gave the well fit with the experimental data for all metal ions (except lead for intraparticle diffusion model) with R^2 values

TABLE 4. The kinetic constants of heavy metals adsorption

Models	Cd	Cu	Ni	Pb	Zn
Pseudo-first order kinetics equation					
k_1 (min^{-1})	0.002	0.002	0.003	0.002	0.001
q_e (mg·g^{-1})	2.499	2.515	3.515	2.385	1.633
R^2 (–)	0.875	0.976	0.870	0.905	0.881
Pseudo-second order kinetics equation					
k_2 (g·mg^{-1}·min^{-1})	0.001	0.001	0.001	0.002	0.001
q_e (mg·g^{-1})	1.788	2.339	2.287	2.200	1.778
R^2 (–)	0.909	0.989	0.969	0.969	0.721
Intraparticle diffusion model					
k_{int} (mg·g^{-1}·min$^{-1/2}$)	0.028	0.044	0.038	–	0.025
R^2 (–)	0.965	0.895	0.915	–	0.877

ranging from 0.989 to 0.870. The linear plots of data were presented for metals with the highest value of R^2 (Fig. 3).

Equilibrium tests

The adsorption equilibrium tests were conducted at different initial solution conditions – at pH of 2.0 and 6.0. The pH values of model solutions influence the amount of heavy metals adsorption. It is well known that surface charge of sorbent can be affected by changing of pH values. For the acidic condition the adsorption processes were on the lower level. The experimental data for heavy metals were correlated with three isotherm models Langmuir, Redlich-Peterson and Temkin. The parameters as well as graphical interpretation of mentioned isotherms are shown in Table 5 and Figure 4.

The amounts of adsorption show non-linear relationship on the equilibrium concentration. Based on Table 5 and coefficient of determination, the Langmuir model gives the best fitting for tests data. The adsorption capacities were estimated to be 2.684 mg·g^{-1} for cadmium, 2.578 mg·g^{-1} for cooper, 3.482 mg·g^{-1} for nickel, 2.592 mg·g^{-1} for lead and 2.253 mg·g^{-1} for zinc. The calculated R^2 were 0.908, 0.906, 0.862, 0.899 and 0.839, respectively. Compared to Langmuir isotherm estimated values of R^2 for Redlich-Peterson model were lower in the range of 0.484–0.720. The graphic interpretation of the experimental data of Pb and Zn for this model was without a solution. The values of β parameter (equal to one) indicate that Langmuir model should be more appropriate (Otun et al. 2006). Moreover, the Temkin isotherm was best fitted with Ni adsorption processes.

In the neutral conditions (pH = 6.0) the processes of heavy metals adsorption were more intense (Table 6 and Fig. 5). The maximum adsorption amount for each metal were higher than in acidic conditions with the values (in mg·g^{-1}) of 3.010, 3.662, 4.430, 3.800 and 4.169 for Cd, Cu, Ni, Pb and Zn, respectively. Based on the coefficient of determination (0.998, 0.986, 0.684, 0.966, 0.984), the Langmuir model allow for the better fit of the test data. The lower adsorption

TABLE 5. Langmuir, Redlich-Peterson and Temkin isotherm parameters (pH = 2.0)

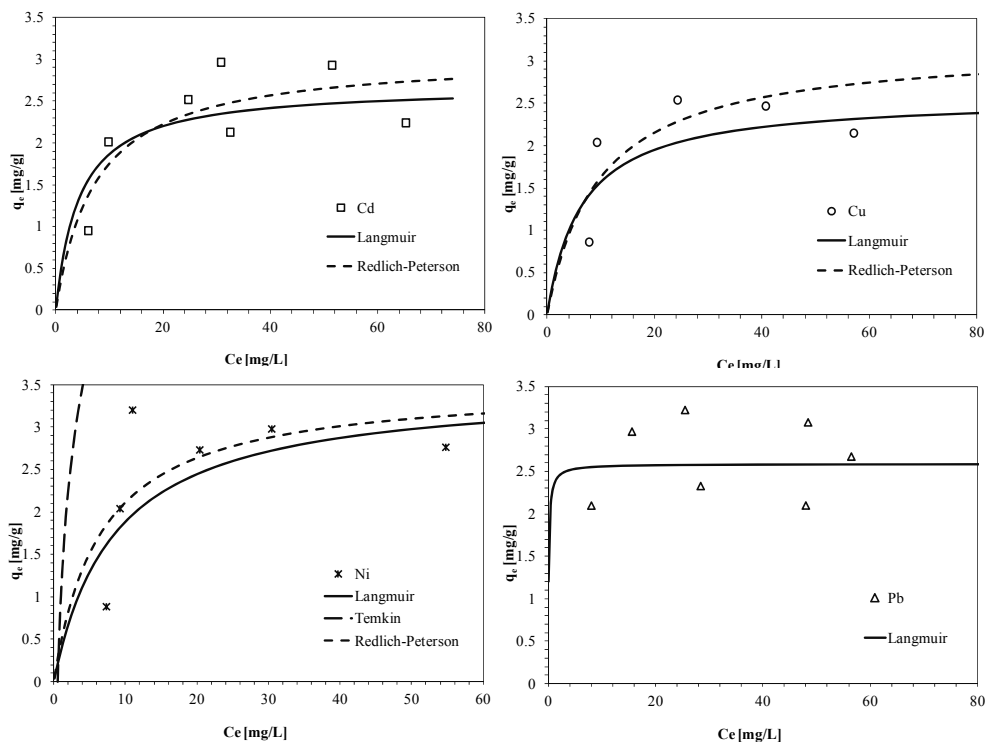| Models	Cd	Cu	Ni	Pb	Zn
Langmuir					
q_{max} (mg·g^{-1})	2.684	2.578	3.482	2.592	2.253
K_L (L·mg^{-1})	0.229	0.156	0.118	8.663	0.197
R^2 (−)	0.908	0.906	0.862	0.899	0.839
R_L (−)	0.038–0.149	0.002–0.007	0.071–0.253	0.003–0.006	0.044–0.167
Redlich-Peterson					
K_R (L·mg^{-1})	0.414	0.333	0.529	−	−
b_R (−)	0.136	0.105	0.151	−	−
β (−)	1.000	1.000	1.000	−	−
R^2 (−)	0.649	0.720	0.484	−	−
Temkin					
A (L·mg^{-1})	−	−	1.767	−	−
B (L·mg^{-1})	−	−	1.774	−	−
R^2 (−)	−	−	0.976	−	−

FIGURE 4. Isothermal adsorption lines for Cd, Cu, Ni, Pb at acidic conditions

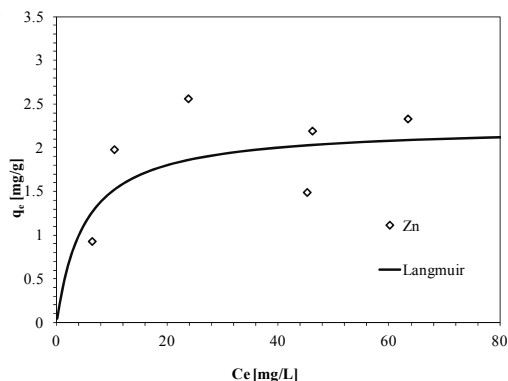FIGURE 4 (continued). Isothermal adsorption lines for Zn at acidic conditions

TABLE 6. Langmuir, Redlich-Peterson and Temkin isotherm parameters (pH = 6.0)

Models	Cd	Cu	Ni	Pb	Zn
Langmuir					
q_{max} (mg·g^{-1})	3.010	3.662	4.430	3.800	4.169
K_L (L·mg^{-1})	8.284	6.924	0.533	7.807	4.618
R^2 (−)	0.998	0.986	0.684	0.966	0.984
R_L (−)	0.001–0.108	0.002–0.126	0.022–0.652	0.002–0.114	0.002–0.178
Redlich-Peterson					
K_R (L·mg^{-1})	29.355	–	10.362	–	–
b_R (−)	12.553	–	5.027	–	–
β (−)	0.923	–	0.719	–	–
R^2 (−)	0.632	–	0.883	–	–
Temkin					
A (L·mg^{-1})	–	–	36.029	–	–
B (L·mg^{-1})	–	–	0.535	–	–
R^2 (−)	–	–	0.813	–	–

capacities in acidic conditions could be attributed to the metal ions competitions with H$^+$ for the binding sites of the reactive material (Nasir et al. 2007). Once more, the adsorption processes of Ni ions were described using the Temkin model, which contains a factor that directly taking into account of adsorbent – adsorbate interactions by ignoring the extremely low and large value of concentrations. The experimental data were not modelled as well using the Redlich-Peterson equation across the concentration range studied. In summary, the heavy metals from solution in acidic and natural conditions were favorably removed by the sorption processes, what may be found in the range of the R_L parameter value (between 0 and 1).
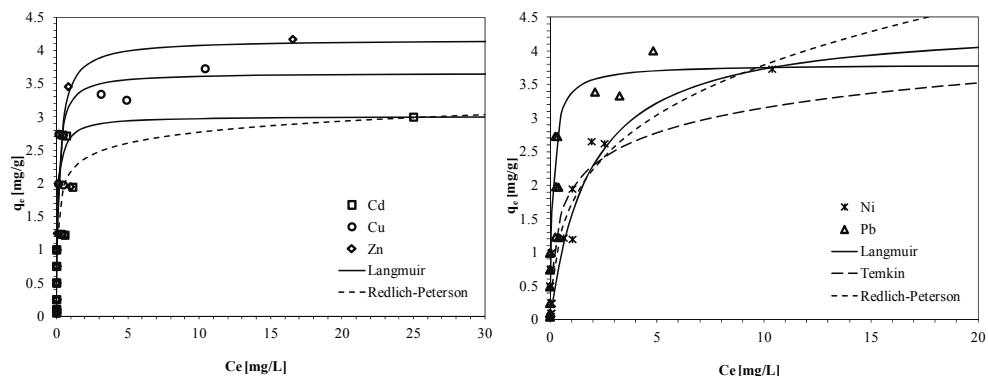
FIGURE 5. Isothermal adsorption lines for Cd, Cu, Ni, Pb and Zn at neutral conditions

CONCLUSIONS

The study presented in this paper has demonstrated that granular activated carbon (GAC) can be used as an effective heavy metals (Cd, Cu, Ni, Pb and Zn) adsorbant from multicomponent aqueous solution in neutral as well as in acidic conditions. The kinetic of heavy metals adsorption followed the pseudo--second order model, the calculated values of coefficient of determination for this model were higher than for pseudo--first order and intraparticle diffusion models. The adsorption processes were slow and evenly distributed over time, the maximum adsorption capacities were achieved in 48 h. The experimental data of adsorption tests were correlated well with the Langmuir isotherm model. In addition, nickel ions adsorption processes were well described using Temkin isotherm (with coefficient of determination R^2 of 0.976 in acidic conditions and of 0.813 in neutral conditions). Furthermore, the adsorption intensity of heavy metals was affected by initial pH of the solutions. Maximum adsorption capacities in neutral conditions were higher (3.010, 3.662, 4.430, 3.800 and 4.169 mg·g^{-1} for Cd, Cu, Ni, Pb and Zn, respectively) than in acidic conditions (2.684, 2.578, 3.482, 2.592 and 2.253 mg·g^{-1}, respectively). Therefore, the occurrence of acid rain can affect the dimensions of PRB treatment zone. The conducted studies provide useful information for GAC application as a reactive material in PRBs protecting groundwater along road infrastructure. Parameters calculated on the basis of test results (equilibrium rate constants and adsorption capacities) are the basis for modelling of contaminants flow through the PRB filled with GAC.

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Streszczenie: *Usuwanie metali ciężkich na węglu aktywowanym – sorpcja równowagowa i kinetyczna.* Węgiel aktywny jest skutecznym sorbentem powszechnie wykorzystywanym do usuwania zanieczyszczeń organicznych i nieorganicznych z roztworów wodnych. W przeprowadzonych doświadczeniach, granulowany węgiel aktywny (GAC) użyto do badania procesów adsorpcji metali ciężkich (Cd, Cu, Ni, Pb i Zn). Badania (typu batch test) przeprowadzono w funkcji czasu, stężenia metali ciężkich i wartości pH. Otrzymane wyniki wskazują na skuteczne usuwanie wyżej wymienionych metali ciężkich z roztworów wodnych. Podczas badań mechanizmu procesów adsorpcyjnych wykorzystano następujące modele kinetyczne: pseudopierwszego, pseudodrugiego rzędu oraz model wewnątrzcząsteczkowy. Ponadto, wyniki otrzymane z badań sorpcji równowagowej zostały opisane następującymi modelami: Langmuira, Redlicha-Petersona i Temkina. Wykorzystując parametry izotermy Langmuira, obliczono wartości maksymalnych zdolności adsorpcji dla metali ciężkich, które wyniosły dla warunków odczynu obojętnego: Cd – 3,010, Cu – 3,662, Ni – 4,430, Pb – 3,800 i Zn – 4,169 mg·g^{-1}, i dla warunków odczynu kwaśnego: Cd – 2,684, Cu –2,578, Ni – 3,482, Pb – 2,592 i Zn – 2,253 mg·g^{-1}.

Słowa kluczowe: węgiel aktywny, metale ciężkie, wody spływowe, adsorpcja

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